

# PATENT ABSTRACTS OF JAPAN

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## (54) NONAQUEOUS SECONDARY BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous secondary battery which is prominent in overcharge safety, reduces self-discharge during high temperature storage and can ensure reliability after the high temperature storage.

SOLUTION: A manufacturing method of the nonaqueous secondary battery uses metal oxide or metal sulfide as anode active materials and carbon materials or materials into which Li can be inserted at cathode. (A) Benzene ring, an alkyl and/or compound bound by halogen atom are included in organic electrolytic solution injected into a battery case as well as (B) monomer material, forming conductive polymer on an anode surface by preliminary charge after assembling a battery, is included in this organic electrolytic solution or anode.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the nonaqueous secondary battery which can secure the reliability after high temperature storage while it is excellent in overcharge safety.

[0002]

[Description of the Prior Art]Since the nonaqueous secondary batteries represented by the lithium ion battery using the material in which the carbon material or Li insertion to a negative electrode is possible using a metallic oxide and metallic sulfide as positive active material are high tension and high energy density, their demand of the is increasing increasingly. However, since safety falls as it becomes high energy density, improvement in safety is also important. In the usual safety measures, since it is in the tendency for an energy density to fall, to improve safety is desired, maintaining an energy density.

[0003]Adding biphenyl (JP,9-171840,A) and cyclohexylbenzene (JP,2001-015155,A), and improving the safety at the time of overcharge in a cell, until now is proposed. According to the above-mentioned additive agent, gas is emitted at the time of overcharge, the current cutoff valve operates easily, and these secure safety with combination with this current cutoff valve.

[0004]

[Problem(s) to be Solved by the Invention]However, by cells, such as a nonaqueous secondary battery which added the above additive agents, especially a square shape, a laminated type, by this invention persons' examination. It turned out that there is a problem of self-discharge becoming large and it becoming impossible to secure the reliability of a cell if it stores especially under an elevated temperature for a long time which stores this by a charging state for a long time.

[0005]An object of this invention is to provide the nonaqueous secondary battery with which the self-discharge at the time of high temperature storage was reduced and which can fully secure the reliability after high temperature storage, while excelling in overcharge safety in the light of such a situation.

[0006]

[Means for Solving the Problem]As a result of this invention persons' inquiring wholeheartedly to the above-mentioned purpose, while adding additive agents, such as cyclohexylbenzene, in organic electrolysis liquid, A monomer substance polymerization-ized by preliminary charging after a cell

assembly in this electrolysis solution or an anode is added, When a coat of a conductive polymer was formed in a positive electrode surface, it finds out that a nonaqueous secondary battery with which it excelled in overcharge safety, and self-discharge at the time of high temperature storage was reduced and which can fully secure reliability after high temperature storage is obtained, and came to complete this invention.

[0007]Namely, in a nonaqueous secondary battery using [ this invention / using a metallic oxide or metallic sulfide as positive active material ] material in which a carbon material or Li insertion to a negative electrode is possible, A nonaqueous secondary battery, wherein a conductive polymer is formed into organic electrolysis liquid in a positive electrode surface, including a compound which an alkyl group and/or a halogen atom combined with A benzene ring is started. It is the compound which an alkyl group combined with the benzene ring by this invention especially in the above-mentioned A ingredient, A nonaqueous secondary battery of the above-mentioned composition which is 3 to 7 % of the weight, and the above-mentioned conductive polymer among organic electrolysis liquid Polypyrrole, They are a nonaqueous secondary battery of the above-mentioned composition which is poly aniline or these derivatives, and a thing which can provide further a nonaqueous secondary battery of the above-mentioned composition whose cell shape is a square shape or a laminated type, respectively.

[0008]While this invention includes a compound which an alkyl group and/or a halogen atom combined with A benzene ring as a manufacturing method of a nonaqueous secondary battery of each above-mentioned composition in organic electrolysis liquid poured in into a cell case, A manufacturing method of a nonaqueous secondary battery including a monomer substance which forms a conductive polymer in a positive electrode surface by preliminary charging after B cell assembly in this organic electrolysis liquid or an anode is started. A manufacturing method of a nonaqueous secondary battery of the above-mentioned composition whose monomer substances of the above-mentioned B ingredient of especially this invention are pyrrole, aniline, or these derivatives, A monomer substance of the above-mentioned B ingredient can provide a manufacturing method of a nonaqueous secondary battery of the above-mentioned composition which is 30 or less % of the weight to a compound which an alkyl group and/or a halogen atom combined with the benzene ring of A ingredient, respectively.

[0009]

[Embodiment of the Invention]Since that by which hydrogen was combined with the carbon coupled directly with the benzene ring among the carbon which constitutes the above-mentioned alkyl group is improvement in overcharge safety, the compound which the alkyl group combined with the benzene ring among A ingredients in this invention is especially desirable. Specifically, cyclohexylbenzene, isopropylbenzene, n-butylbenzene, octylbenzene, toluene, xylene, etc. are mentioned. Also in these, that whose alkyl group especially combined with the benzene ring is the structure where four or more carbon numbers and a long thing are desirable, and the above-mentioned alkyl group has branching structure etc., and it is bulky in three dimensions is desirable, and cyclohexylbenzene is especially desirable. To the compound which the halogen atom combined with the benzene ring. The compound which there are a thing [ benzene / a fluorobenzene, / difluoro] etc. which halogen atoms, such as a fluorine atom and a chlorine atom, combined with the compound which the alkyl group combined with the above mentioned benzene ring further, and especially the fluorine atom combined is desirable.

[0010]As an addition of the compound of such an A ingredient, it is more preferably good 3% of the weight or more, in order to obtain a good result to overcharge safety among organic electrolysis liquid that it is 4 % of the weight or more still more preferably 2.5% of the weight or more 1% of the weight or more. It is preferably good among organic electrolysis liquid that it is 6 or less % of the weight more preferably 7 or less % of the weight 10 or less % of the weight because of reduction of the self-discharge at the time of high temperature storage.

[0011]By this invention persons' examination, if it is in the battery construction of this invention, If it adds among organic electrolysis liquid in 3 to 7% of the weight of the range, especially 4 to 6% of the weight of the range, the compound in which the alkyl group combined the compound of the above-mentioned A ingredient especially with the benzene ring, Can both especially satisfy highly overcharge safety and the low self-discharge nature at the time of high temperature storage, and about overcharge safety. Even if it was a nonaqueous secondary battery of the cell shape of a square shape or a laminated type which does not usually have a current cutoff valve, it turned out that overcharge safety is [ by which the outstanding effect is done so ] fully securable.

[0012]While the compound of the above-mentioned A ingredient is included at an above-mentioned rate in organic electrolysis liquid, in this invention, it is characterized by forming a conductive polymer in a positive electrode surface, and by this conductive polymer. It becomes possible to obtain the nonaqueous secondary battery with which the self-discharge at the time of high temperature storage was reduced and which can fully secure the reliability after high temperature storage. As the above-mentioned conductive polymer, polypyrrole, poly aniline, or these derivatives are mentioned. Although the reason the above-mentioned effect is done so by formation of such a conductive polymer is not clear, the active site of a positive electrode surface is covered by the above-mentioned conductive polymer, and it is considered for controlling the phenomenon in which the compound of the above-mentioned A ingredient reacted and carries out self-discharge in a positive electrode surface.

[0013]Although the method in particular of forming a conductive polymer in a positive electrode surface is not limited in this invention but arbitrary methods can be adopted, It is good to adopt the method of including the monomer substance for conductive polymer formation as a B ingredient in organic electrolysis liquid or an anode, and polymerization-izing this by the preliminary charging after a cell assembly preferably. If the above-mentioned conductive polymers are polypyrrole, poly aniline, or these derivatives, pyrrole, aniline, or these derivatives will be used as the above-mentioned monomer substance. There are methylpyrrole, phenylpyrrole, dimethylaniline, phenylaniline, diphenylaniline, etc. in the above-mentioned derivative. Also in these, what has the few generation of gas is desirable at the time of a polymerization, and the thing which divided and was replaced by atoms and bases other than a hydrogen atom without the generation of gas etc. in a nitrogen atom, especially an aromatic substitution object are desirable.

[0014]Since it will become bulging of a cell, and a cause of an impedance rise if such a monomer substance of B ingredient has too much this, it is preferably [ to the compound of A ingredient ] good [ a substance ] more preferably that it is 2.5 or less % of the weight most preferably 10 or less % of the weight 30 or less % of the weight. since said effect will not be acquired if too small, it is preferably [ to the compound of A ingredient ] good more preferably that it is 2 % of the weight or more most preferably 1% of the weight or more 0.1% of the weight or more. After polymerization-izing of such a monomer substance, if a cell is disassembled and a positive electrode surface is observed and

analyzed, it can check that the coat of a conductive polymer is formed in a positive electrode surface. [0015] In this invention, what dissolved lithium salt in the organic solvent as an electrolyte is used as organic electrolysis liquid in which the compound of the above-mentioned A ingredient, or this and the monomer substance of the above-mentioned B ingredient is included. As an electrolyte, polymers and a solid can also be used by a case. In the above-mentioned organic solvent, ethylene carbonate, PIROPIREN carbonate, Carbonic ester, such as butylene carbonate, dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, and ester species, such as gamma-butyrolactone methyl acetate, are used as a main solvent.

[0016] As other solvents, organic solvents, such as sulfur compounds, such as ether, such as 1,3-dioxolane and 1,2-dimethoxyethane, and sulfolane, a nitrogen-containing compound, a silicon-containing compound, a fluorine-containing compound, and a phosphorus-containing compound, are also used. It is desirable to dissolve the compound which has  $-\text{SO}_2$  combination further, and the compound which has  $-\text{O}-\text{SO}_2$  combination especially in these organic solvents. Specifically, they are a 1,3-propane sultone, methylethyl sulfonate, diethyl sulfate, etc. These compounds are good among an organic solvent for considering it as the amount of 0.5 to 10 % of the weight used to consider it as the amount of 1 to 5 % of the weight used preferably at best especially.

[0017] In lithium salt which is an electrolyte,  $\text{LiPF}_6$ ,  $\text{F}_{2n \text{ of } \text{LiC}_{n+1}\text{SO}_3}$  ( $n > 1$ ), There are  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{NLi}(\text{C}(\text{F}_{2n \text{ of } \text{C}_{n+1}\text{SO}_2})_m \text{F}_{2m+1}\text{SO}_2)$  ( $m, n \geq 1$ ), etc. Otherwise, it is  $\text{RfOSO}_2$   $\text{NLi}$ . [Rf is an alkyl group containing with a carbon numbers of two or more halogen, and two Rf may be the same, it may differ, and, in combination, the shape of for example, polymer, Rf may combine with each other.] It can \*\*\*\*\* and  $\{\text{CH}_2(\text{CF}_2)_4\text{CH}_2\text{OSO}_2\text{N}(\text{Li})\text{SO}_2\text{O}\}_n$  ( $n$ : integer) is mentioned as an example. In these, with  $\text{LiPF}_6$  and a carbon numbers of two or more fluorine-containing organicity lithium salt is desirable especially. Lithium salt is usually used at a rate of 0.1-2 mol/l. among an organic solvent. [0018] In this invention, to positive active material, lithium cobalt oxides, such as  $\text{LiCoO}_2$ , Metallic sulfide, such as metallic oxides, such as lithium nickel oxides, such as lithium manganic acid ghosts, such as  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiNiO}_2$ , manganese dioxide, vanadium pentoxide, and a chromium oxidation thing, titanium disulfide, molybdenum disulfide, is used. What made current collecting materials, such as aluminum foil, the core material, and made the Plastic solid to them is used in the positive electrode mixture in which the anode added suitably binders, such as an electric conduction auxiliary agent and polyvinylidene fluoride, etc. to such positive active material. What uses especially the positive active material which becomes more than 4.2V on Li standard when it charges like  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMn}_2\text{O}_4$  is desirable. That to which the open circuit voltage after a charge end used as positive active material the lithium multiple oxide in which more than 4.3V is shown on Li standard is desirable.

[0019] Carbon, such as black lead, such as KS6 [crystalline / high], and low crystalline carbon black, is used for the electric conduction auxiliary agent of an anode. Since too much quantity of an electric conduction auxiliary agent will cause the generation of gas if a battery characteristic will fall if too small, and there is although few directions can reduce reactivity with the organic electrolysis liquid in

a charging state, it is preferably good among positive electrode mixture that it is 2 to 2.5 % of the weight more preferably 1.5 to 3% of the weight one to 5% of the weight. As for the rate of low crystalline carbon, it is preferably good among the whole electric conduction auxiliary agent that it is 70 to 80 % of the weight 50 to 90% of the weight. When there is little quantity of an electric conduction auxiliary agent, and the use rate of high crystalline black lead is high, it is in the tendency for an electrical property to fall.

[0020]In this invention, a negative electrode usually distributes to a solvent what added the electric conduction auxiliary agent to the above-mentioned material by the binder and the case coming [ a carbon material or the material in which Li insertion is possible ] to use, and what applied this to current collecting materials, such as copper foil, and the Plastic solid was made after desiccation is used. The metallic compounds (for example,  $\text{SnO}_x$ ,  $\text{SiO}_x$ , etc.) containing tin and silicon are used for the material in which the above-mentioned Li insertion is possible as a metallic oxide, and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  etc. are used for it as metal nitride.

[0021]In this invention, make various publicly known separators intervene among two poles, and it loads with an above-mentioned anode and negative electrode into a cell case, And after including the compound of A ingredient in the organic electrolysis liquid poured into this, including the monomer substance of B ingredient in this organic electrolysis liquid or an anode further and assembling a cell, preliminary charging is carried out, the above-mentioned monomer substance is polymerization-ized, and it is considered as the nonaqueous secondary battery with which the conductive polymer was formed in the positive electrode surface.

[0022]The nonaqueous secondary battery of this invention has especially a large effect of this invention, when it is made into the cell gestalt of a square shape or a laminated type. However, it is good also as other gestalten of various kinds of, such as telescopic, a button type, and a coin type, and there is no limitation in particular in a cell gestalt.

[0023]

[Example]Below the example of this invention is indicated and it explains to it more concretely. However, this invention is not limited only to the following examples.

[0024]Example 1 -- first, after dissolving  $\text{LiPF}_6$  in ethylene carbonate, methylethyl carbonate was added, it mixed and 1.2 mol/l. of  $\text{LiPF}_6$  was dissolved in the mixed solvent of the volume ratios 1/2 of ethylene carbonate and methylethyl carbonate. Further, cyclohexylbenzene (compound of A ingredient) was dissolved 4% of the weight, 0.2 % of the weight and also a 1,3-propane sultone were dissolved for phenylpyrrole (monomer substance of B ingredient) in this 2% of the weight as an additive agent, and organic electrolysis liquid was prepared.

[0025]Next, added 0.5 % of the weight of black lead, and 2 % of the weight of carbon black to 93.5 % of the weight of  $\text{LiCoO}_2$ , mixed, the solution made to dissolve 4% of the weight of polyvinylidene fluoride in N-methyl pyrrolidone beforehand was made to distribute this, and it was considered as the positive electrode mixture slurry. After applying this positive electrode mixture slurry to both sides of aluminium foil with a thickness [ as a positive pole collector ] of 15 micrometers uniformly (however, it did not apply to the negative-electrode and most-inner-circumference inner surface side which does not counter), it is dried.

Then, compression molding was carried out with the roller press machine, welding of the lead body was performed after cutting in a predetermined size, and the band-like anode was produced.

[0026] Apart from this, the solution dissolved in N-methyl pyrrolidone was made to distribute 5% of the weight of polyvinylidene fluoride beforehand, and 95 % of the weight of meso-carbon-micro-beads baking bodies were made into the negative electrode mixture slurry. After applying this to both sides of band-like copper foil with a thickness [ as a negative pole collector ] of 10 micrometers (however, it did not apply to the anode and outermost periphery outside surface side which does not counter), it is dried.

Then, compression molding was carried out with the roller press machine, welding of the lead body was performed after cutting in a predetermined size, and the band-like negative electrode was produced.

[0027] Next, the collecting tab was attached to each of the above-mentioned anode and a negative electrode, those anodes and negative electrodes were piled up and wound via the separator which consists of a 20-micrometer-thick microporous polyethylene film, and it was considered as the electrode body. Insulating tape was attached to this, it inserted into the cell case whose size is 5mmx30mmx48mm, and welding of a lead body and laser welding of the battery lid to the open end of a cell case were performed. Preliminary charging was performed and the appropriate back produced the square-shaped nonaqueous secondary battery, after having poured in the aforementioned organic electrolysis liquid into the cell case, closing the above-mentioned electrolysis solution inlet after this pouring and making the inside of a cell into a sealed state from the electrolysis solution inlet established in the battery lid.

[0028] Drawing 1 is a mimetic diagram of the nonaqueous secondary battery of the square shape produced in this way. As for one, a negative electrode and 3 are separators an anode and 2 among a figure. In order to avoid complicated-ization, the used charge collector is not illustrated in production of the anode 1 or the negative electrode 2. 4 is a cell case made from aluminum, and serves as the negative pole terminal. The electrode body and organic electrolysis liquid of flat shape swirl structure which consist of the anode 1, the negative electrode 2, and the separator 3 are stored in the above-mentioned cell case 4. From the electrode body 6 of the flat shape swirl structure which the insulator 5 which consists of polytetrafluoroethylene sheets is arranged, and becomes a pars basilaris ossis occipitalis of the cell case 4 from the aforementioned anode 1, the negative electrode 2, and the separator 3. The positive electrode lead object 7 and the negative electrode lead object 8 of the anode 1 and the negative electrode 2 which were connected to the end, respectively are pulled out. The terminal 11 made from stainless steel is attached to the cover plate 9 made from an aluminum alloy which obturates the opening of the cell case 4 via the insulating packing 10 made from polypropylene, and the lead board 13 made from stainless steel is attached to it via the insulator 12 at this terminal 11. By inserting the above-mentioned cover plate 9 in the opening of the cell case 4, and welding both joined part, the opening of the cell case 4 is obturated and the inside of a cell is sealed. This nonaqueous secondary battery was disassembled and it checked that the conductive polymer was formed from the result of having analyzed some coats of the above-mentioned electrode.

[0029] The square-shaped nonaqueous secondary battery was produced like Example 1 except not

having added phenylpyrrole in comparative example 1 organic-electrolysis liquid.

[0030]The square-shaped nonaqueous secondary battery was produced like Example 1 except not having added cyclohexylbenzene in comparative example 2 organic-electrolysis liquid.

[0031]About each nonaqueous secondary battery of the above-mentioned Example 1 and the comparative examples 1 and 2, overcharge safety study and a storage examination were done, and battery capacity was evaluated by the following method. These results were as being shown in Table 1.

[0032]<Overcharge safety study> Each cell is made to discharge to 3.0V by 1CmA at a room temperature, and it discharged by 4.2V by 1C, and was made to discharge to 3.0 by 0.2CmA after 2.5-hour charge by CCCV first. When it charged to 4.2V, anode potential was 4.3V on Li standard. As overcharge safety study, the cell was made into the 2.5-hour charge back, and it overcharged [ 1CmA ] by 0.5A, 1A, 2A, and 5A by making 6V into upper limit voltage by 4.2V and CCCV. The skin temperature of the cell made the maximum current which was 135 \*\* or less the overcharge safe current value.

[0033]It discharges by 4.2V by 1CmA, and the <storage examination> cell was made to discharge to 3.0V by 1CmA after 2.5-hour charge by CCCV (capacity at this time is set to X). Then, 4.2V was performed by 1CmA and charge was performed by CCCV for 2.5 hours. A 60 \*\* thermostat was made to discharge to 3.0V by 1CmA after storage for 20 days after that furthermore (capacity at this time is set to Y). It is rate of self-discharge (%) = from such capacity X and Y.  $[(X-Y) / X] \times 100$  was calculated by calculation.

[0034]

表 1

	過充電安全電流値 (A)	自己放電率 (%)
実施例 1	5 以上	2 0
比較例 1	5 以上	2 8
比較例 2	0. 5	2 2

[0035]The cell of Example 1 improving overcharge safety 10 or more times from the result of the above-mentioned table 1 compared with the cell of the comparative example 2 in which only the monomer substance of B ingredient was included and the compound of A ingredient was not included. The self-discharge at the time of high temperature storage can be suppressed, and it turns out that it is what can also secure the reliability after high temperature storage. On the other hand, even if the cell of the comparative example 1 in which only the compound of A ingredient was included and the monomer substance of B ingredient was not included could satisfy overcharge safety, the self-discharge at the time of high temperature storage increased, and it was not able to secure reliability after high temperature storage.

[0036]

[Effect of the Invention]As mentioned above, in this invention, a metallic oxide or metallic sulfide is used as positive active material, While including the compound which the alkyl group and/or the



halogen atom combined with the benzene ring as an A ingredient in organic electrolysis liquid in the negative electrode using a carbon material or the material in which Li insertion is possible, it had composition of forming a conductive polymer in a positive electrode surface.

Therefore, the nonaqueous secondary battery which is excellent in overcharge safety and is moreover excellent in the reliability after high temperature storage can be provided.

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[Translation done.]